THERMO-ELECTRIC PHENOMENA AND ELECTRICAL RESISTANCE IN SINGLE METAL CRYSTALS.

BY P. W. BRIDGMAN.
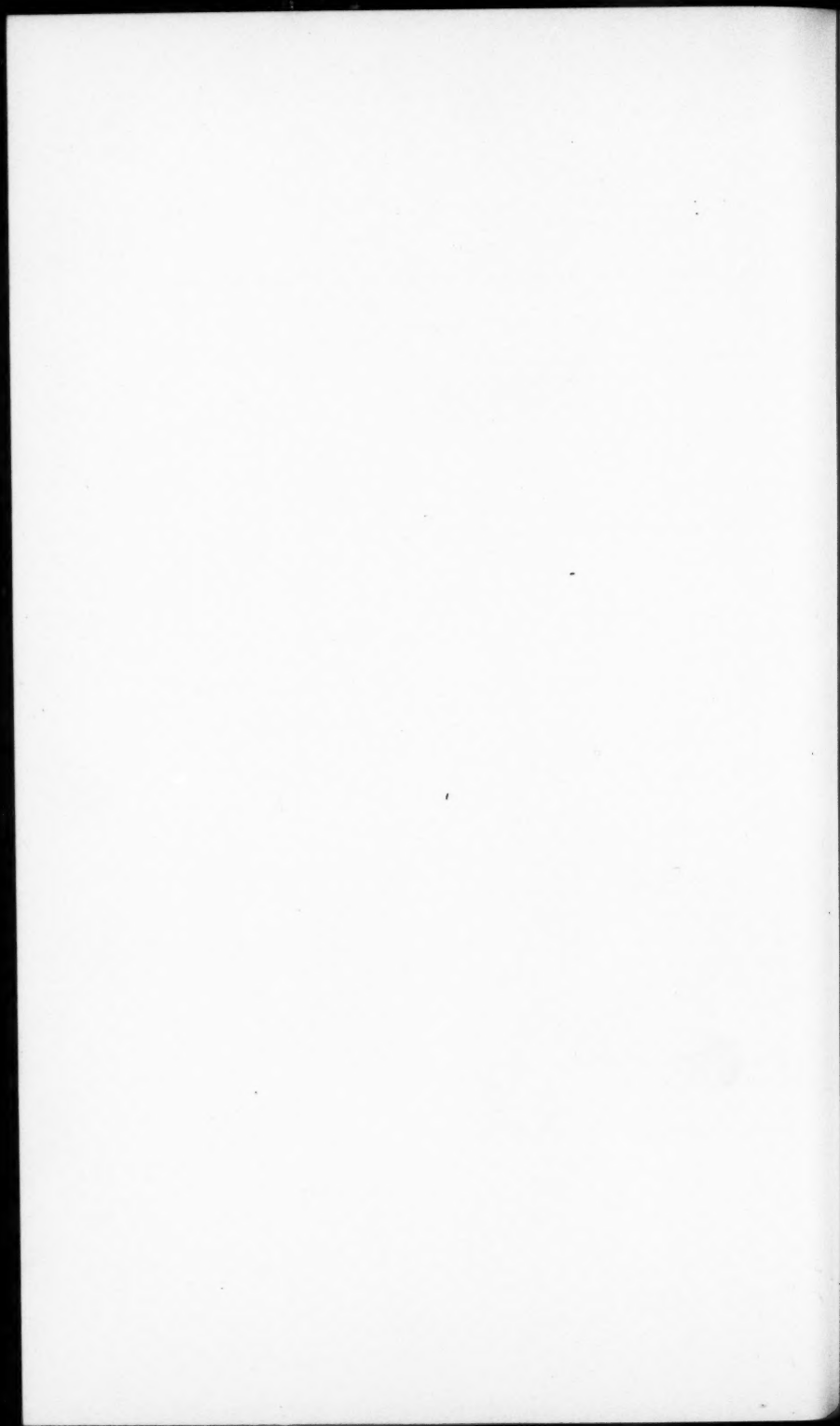
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P. W. BRIDGMAN.

CONTENTS.

INTRODUCTION.

In 1926 I published a paper[1] containing, in addition to some other matters, data for the thermal e.m.f. of single crystals of Zn, Bi, Cd, Sn, Sb, and Te as a function of the crystal orientation. The results thus obtained were not as complete or as accurate as could have been desired, the number of specimens being comparatively small, and in several cases the range of orientation being narrow. For example, the orientation of the specimens of Bi varied through only 22° instead of through the full 90°. A number of significant conclusions could be drawn from the data of that paper, but there were some important questions, as, for example, the precise way in which thermo-electric symmetry departs from Kelvin's relation (if indeed it departs at all), which could not receive a certain answer from the measurements. Furthermore, Linder[2] has also published thermo-

electric data for single crystals, from which he draws conclusions not always the same as mine, so that a reëxamination was desirable.

In this paper improved results are obtained. In the first place, the method of producing single crystals has been much improved, so that it is now possible to cover the entire range of orientation, and in the second place, the apparatus by which thermo-electric force is measured has been improved so that now measurements can be made simultaneously with 16 different specimens, practically the only variable being the crystal orientation. This paper contains these new data, and a reëxamination, in their light, of the question of the symmetry relations. I have also remeasured, since the new specimens were better adapted to this purpose than the old ones, and since results disagreeing with my early ones have been since published by Schneider,[3] the specific resistance of most of these metals as a function of direction. I have further taken advantage of the new material to measure the effect of pressure on the resistance of Sb and Bi over the entire range of orientation.

The Method of Producing Single Crystals.

The new method is a modification of that used before;[4] this consisted in lowering a mold containing the molten metal slowly through the bottom of a furnace maintained at a constant temperature above the melting point. If the rate of lowering is enough less than the rate of crystallization, the liquid solidifies in a continuation of the crystal lattice already laid down, and if solidification can be forced to start as a single crystal grain, as by making the lower end of the mold taper to a sharp point, the mold becomes filled, after solidification, with a single crystal grain. In the previous work the largest furnace used had an interior diameter of about 2.5 cm., so that this was the greatest diameter of any crystal that could be made. The control of the orientation of the crystal was the difficult feature of the previous work. The crystals show a striking inclination to grow with the planes of easiest cleavage parallel to the vertical axis of the furnace; there is, however, considerable haphazard variation from this preferred direction, and by making a large number of castings, it was possible to cover a considerable range of orientation. The range depends to a marked degree on the nature of the metal. The direction of growth was much less strongly preferential in rods of small diameter than in the larger rods.

The new method depends on the use of a furnace of 10 cm. internal

diameter, against the former 2.5. This makes it possible to use a
mold consisting of criss-cross arms of glass tubing (a photograph
of such a mold is shown in Figure 1), arranged at a variety of angles.
If the rate of lowering is slow enough, the mold, as before, becomes
filled with a single crystal grain. By breaking the mold at the cor-
ners of the arms, one has effectively a number of short crystal rods
of a variety of orientations out of a single crystal. Of course this
method does not give control of the orientation of any individual
rod, but it does ensure that the orientation of the aggregate of rods
is spaced over the entire range, which is the essential thing. The
molds may be made of any desired degree of complication; my as-
sistant, Mr. Philip Dalton, developed much skill in making them,
and produced molds with as many as 50 arms. I myself was usually
satisfied with more modest molds of 12 arms that could be made
simply from a single length of tubing, bent first into a hairpin at
the middle, and then the two arms of the hairpin bent to the desired
angles.

Various new devices of manipulation were used. One of the most
important matters is the deposition of some kind of a coating on the
inside of the glass, to prevent the metal from sticking to the glass,
and to allow the easy removal of the glass by cracking. If the mold
is not coated in some way, the sticking is so bad as to make quite
impossible the removal of the glass without mechanical deformation
of the metal inside; this is particularly serious when the diameter of
the castings is small, as here. Formerly, the tube had been washed
with a dilute solution of Nujol in petroleum ether, and then dried
by heating in vacuum; this left enough deposit to accomplish the
purpose. It was, however, difficult to control the operations ex-
actly, and failures were numerous, either because the deposit had
been entirely oxidized away, or because so thick a deposit was left
that gas bubbles were generated in sufficient number to break the
continuity of the castings. The new material used for coating the
molds was an enamel made by the General Electric Co. for insu-
lating copper wire. This was made very dilute with $CHCl_3$, the
interior of the mold was washed with it, allowed to drain in a vertical
position for several hours, and then the mold was heated progres-
sively with a Bunsen burner, first driving off the volatile matter,
and then carbonizing the residue, which was left on the inner walls
as a black deposit of carbon. The thickness of this deposit was
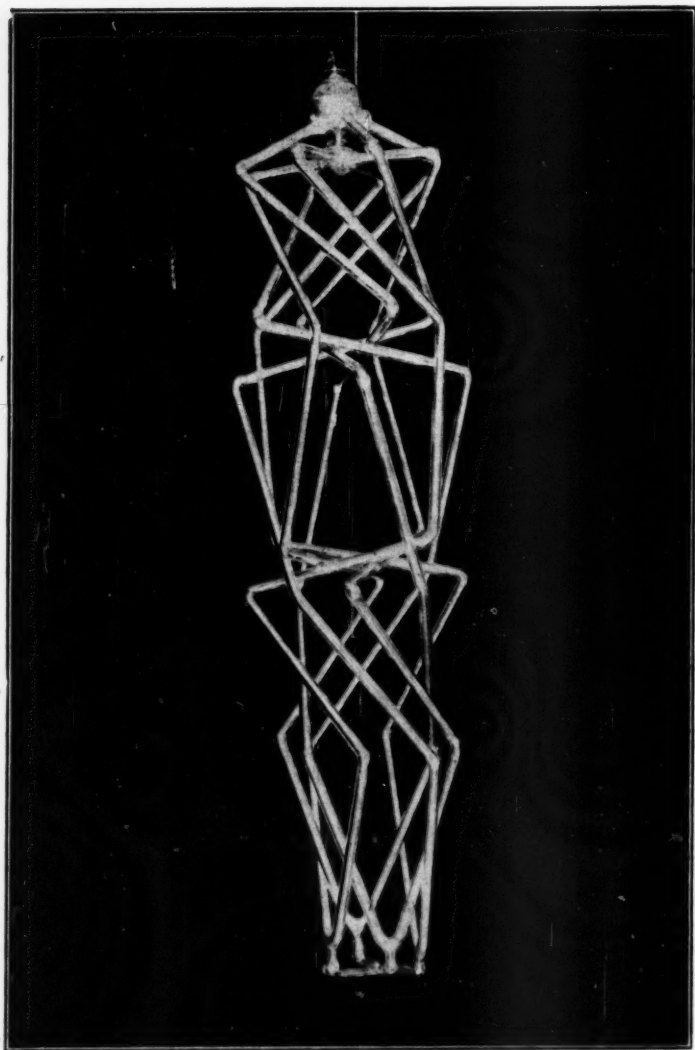now appropriately reduced by heating the entire mold in an electric

FIGURE 1. Photograph of the glass mold in which many single crystal rods with a wide range of orientation may be cast in one operation.

furnace to a temperature of 400° or 500°. If the mold is sealed to prevent oxidation, the deposit is unaffected by this treatment, but if air is allowed to enter, the deposit is oxidized and completely disappears in the course of 10 minutes or so. By controlling the amount of air and the time of heating, the deposit may be reduced to such a thickness that there is a just perceptible blackening of the walls, which is the ideal to strive for.

Filling the mold with molten metal could be accomplished in various ways; the diameter of the glass tubes used was so small that the metal mensicus would not break, even in an inverted position. It was therefore possible, when convenient, to fill the mold from an upper chamber, allowing the molten metal to run down one arm and up the other with no danger of gas bubbles breaking the continuity. In some cases I found it convenient to fill by sucking the molten metal up into the mold from an open lower reservoir. I had used this method some time ago in preliminary work, and it has been recently described in a publication by Sachs.[5] I found it necessary to suck the metal up very slowly, otherwise gas bubbles were apt to appear. The rate of rise may be made as slow as desired by connecting the upper end of the mold to a large vessel, which is exhausted very slowly through a fine capillary attached to the vacuum pump. To prevent the metal in the open reservoir from oxidizing during the filling, the furnace may be filled with an atmosphere of CO_2.

The Apparatus for Measuring Thermal e.m.f.

The previous apparatus consisted of two temperature baths at different temperatures, with the single crystal rods leading from one bath to the other, and with copper leads soldered to the ends of the crystals. The e.m.f. was measured as a function of the temperature difference. The apparatus could be used with only one crystal rod at a time, so that besides the disadvantage of slowness, slight temperature irregularities in the different runs might superpose vagaries on the differences due to differences of orientation in the different specimens. The new apparatus was so designed that 16 different samples could be measured with a single set-up, thus very much increasing the speed, and decreasing any error due to temperature irregularities. The 16 crystal rods, each about 3 mm. in diameter and about 7.5 cm. long, were passed through small stuffing boxes, arranged in a row in a block of bakelite 2.5 cm. thick. This block of bakelite was clamped, between asbestos packing, between two

heavy cast brass cylinders about 7 cm. inside diameter, provided with openings with machined faces to press against the bakelite. A section is shown in Figure 2 and an elevation in Figure 3.   The
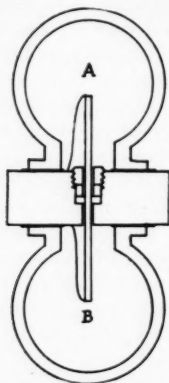

FIGURE 2.   Section of part of the apparatus for measuring thermal e.m.f. of single crystal rods.   The rod reaches from A to B.   The two ends A and B are maintained at different temperatures by two streams of oil, circulated through two regulated sources.

dimensions are such that the ends of the crystal rods project to about the middle of the brass cylinders.   The cylindrical brass castings are connected at top and bottom to two separate reservoirs, each filled with kerosene.   A rapid circulation is maintained through the cylindrical castings, past the projecting ends of the crystals, into the reservoirs at the top and into the castings at the bottom. The reservoirs are maintained at different constant temperatures by thermostatically controlled electric heating arrangements.   In addition to the stirrers at the upper ends of the castings, the reservoirs also have independent stirrers, in order to keep the temperature as uniform as possible.   One of the baths was maintained at a constant temperature of about 20°.   Since sometimes the room rose above this temperature, artificial cooling was maintained by a current of tap water circulating through a coil of copper tube placed in the reservoir.   The thermostatic control with electric heating was superposed on this constant cooling.   The other bath was varied in temperature, the temperatures chosen being 37°, 54°,
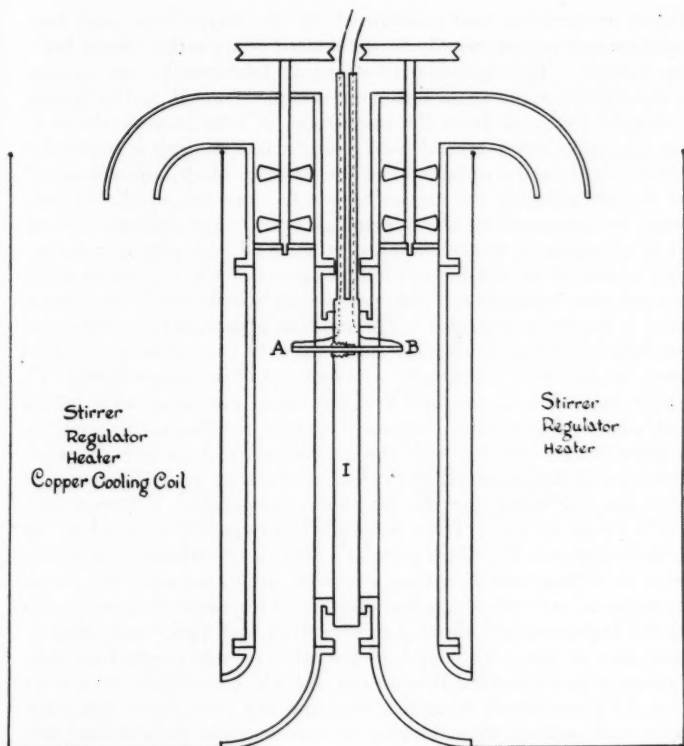
FIGURE 3. Section in elevation of part of the apparatus for measuring thermal e.m.f. of single crystal rods. There is provision for measuring 16 rods at the same time. A single sample rod is shown at AB. The others are mounted in a similar way in the rest of the bakelite block I.

70°, and 88°. Temperatures were read with calibrated mercury-in-glass thermometers. The temperature regulator was a conventional mercury-in-glass affair; four of these regulators were used, each set permanently to one of the four temperatures. After readings at one temperature had been completed, the regulator for the next

higher temperature was substituted for the former one, and temperature was run up rapidly to the desired point with a heavy heating current. The operation of changing temperature and coming to equilibrium again at the new point occupied from 10 to 15 minutes.

Copper leads, all from the same spool of wire, were soldered to the two ends of the crystal rods, brought out through a stand-pipe arrangement at the upper end of the bakelite block, and connected to the arrangement for measuring e.m.f. Any one of the 16 rods could be connected to the measuring arrangement through a bank of 32 all-copper switches, mounted in a closed box, and operated by long handles from outside to eliminate parasitic e.m.f.'s due to slight temperature inequalities. The circuit by which e.m.f. was measured is shown in Figure 4. The method is essentially a deflection method, this being much more rapid than the potentiometer method used before, and sufficiently accurate. A Pye galvanometer, G, which has a low period and a steady zero, was used, with mirror and scale. The circuit contained various resistances in series or in parallel, R_1 and R_2, with the galvanometer, by which its sensitivity could be appropriately varied, so that for each different sort of metal the throw for the maximum temperature difference was made about 40 cm. There were also arrangements by which an acid Weston cell, E_1, which permits a fairly large current to be drawn from it without deterioration, could be connected into the circuit in order to calibrate the galvanometer. This calibration was made at the beginning and the end of every run and varied only slightly from day to day. The e.m.f. of the acid cell was checked by comparison with a standard Weston cell, E_2, which could also be thrown into the same circuit in such a way that the comparison was made by a null method, thus drawing no current from the standard cell. R_3, which is a decade box reaching to 10,000 ohms in steps of 1 ohm, and R_4, which reaches to 100,000 in steps of 10,000, were used in making the various calibrations. Error from galvanometer drift and parasitic e.m.f.'s in parts of the apparatus beyond the thermocouple switch were limited by using the double throw of the galvanometer, instead of its deflection from rest. The period of the galvanometer was of the order of 5 seconds, so that it was possible to complete the measurements on a single rod in 20 seconds or less, and the entire series in 5 minutes. Constancy of the bath temperature was checked by repeating at the end of the series the measurement on the first couple; this also checked whether temperature equilibrium had been attained before beginning the run.
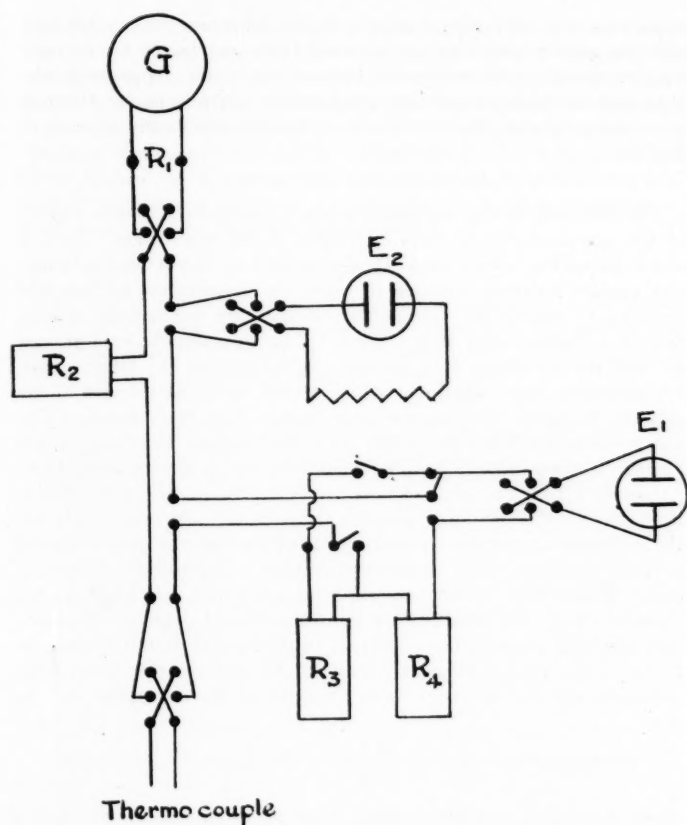
Figure 4. The circuits for measuring thermal e.m.f.

Before the adoption of the method just described, another piece of apparatus was built and tested, in which 16 crystal rods were led between two heavy copper bars, 5 cm. on a side, maintained at different temperatures. The crystal rods dipped into wells drilled in the copper bars, filled with stagnant oil, and of a diameter only slightly greater than that of the rods. The difficulty with this

apparatus was that temperature equality between the crystal bars
and the copper bars was not attained; this was tested by thermo-
couples directly soldered to the ends of the rods. Apparently the
only way by which a positive temperature control can be attained
is to immerse the crystal rods in a rapidly circulating stream of
liquid.

METHODS OF CALCULATION.

The first step in the computation was to reduce the double throws
of the galvanometer to volts by means of the calibration. Next a
small correction, which could be determined by linear interpolation,
was applied to these voltages to bring the temperature of the cold
junction to exactly 20°; the actual temperature was usually a frac-
tion of a degree below this. Then, by linear interpolation between
20° and the maximum temperature, the voltages at the intermediate
temperatures were calculated which would have been found if the
relation between temperature and voltage had been linear. The
difference between the linear and the actual voltage was then plotted
against temperature. The difference curve was, in almost every case,
parabolic within the error of measurement; the condition for this is
that the curve should be symmetrical about the mid point and that
the ordinates at the one-quarter and the three-quarter points should
be three-quarters of the maximum ordinate. A parabolic difference
curve means that within experimental error the relation between
thermal e.m.f. and temperature is of the second degree. The con-
stants in this second degree relation could then be found at once in
terms of the total voltage, e_0, between 20° and the maximum tem-
perature, and the deviation from linearity at the mid point, Δ. In
fact:

$$\text{(thermal e.m.f.)} = \left(\frac{e_0 + 4\Delta}{t_0} \right) (\tau - 293.1) - \frac{4\Delta}{t_0^2} (\tau - 293.1)^2,$$

where t_0 is the temperature range from 20° to the maximum, and τ
is Abs. temperature.

If Kelvin's relation holds, that is, if at every temperature the
thermal e.m.f. of a crystal rod against any homogeneous substance
is a linear function of $\cos^2\theta$, θ being the angle between the length
of the rod and the crystal axis, it is evident that e_0 and Δ must also
be linear functions of $\cos^2\theta$. e_0 and Δ were accordingly plotted against
$\cos^2\theta$, and the best smooth curve drawn through the points. If the
relation turned out to be linear, then the values of e_0 and Δ at the

extreme points, that is, for $\cos\theta = 1$ and $\cos\theta = 0$, were read from the curve. From the e_0 and Δ found in this way the values of the constants in the two-power series in temperature for thermal e.m.f. against copper could be calculated at the two extreme orientations. From the series formula the Peltier heat against copper and the Thomson heat can be found by differentiation. If e_0 or Δ was not linear against $\cos^2\theta$, as was the case for two metals, then the procedure just described must be repeated at enough orientations between $0°$ and $90°$ to define the behavior.

DETAILED DATA.

Zinc. The material was Kahlbaum's best zinc. A considerable number of castings were made: of these there were two sets in two many-arm molds with from 30 to 50 orientations, and at least five castings in the simpler mold with 12 orientations.
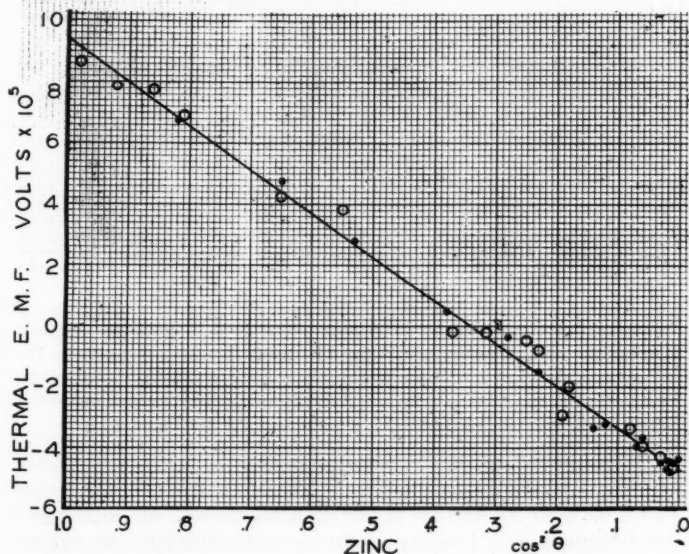

FIGURE 5.   Thermal e.m.f. of single crystal zinc against copper between $20°$ and $88°$ C.   The abscissa is the square of the cosine of the angle between the length of the rod and the principal crystal axis.

Measurements of thermal e.m.f. were made on two sets of 16
rods, one set from each of the larger molds, selected to cover as
uniformly as possible the entire orientation range. The angle of
the basal plane with the length was determined by cleavage, but
instead of cleaving at room temperature, the rod was cooled in liquid
air and cleaved while still cold by pressing into it the point of a knife.
This trick of cleaving in liquid air is due to Boydston;[6] it is well worth
while, the cleavage being much easier to produce and much sharper,
and there being less danger of bending the rod.
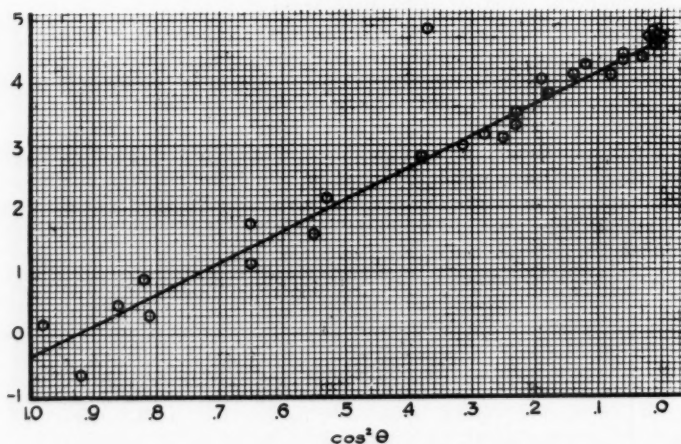
FIGURE 6. Shows the deviation from linearity in the relation between
temperature and thermal e.m.f. of single crystal zinc against copper. The
deviation is shown in 10^{-6} volts at the mean temperature 54°, the tempera-
ture range being from 20° to 88° C. The abscissa is the square of the cosine
of the angle between the length of the rod and the crystal axis.

The results of the measurements of thermal e.m.f. are plotted
in Figure 5 and Figure 6; in Figure 5 the total e.m.f. of the couple
Zn-Cu between 20° and 88° is plotted against $\cos^2\theta$, and in Figure 6
the deviations from linearity at the mean temperature also against
$\cos^2\theta$. All the e_0's of one set of rods have been corrected by the
constant amount, 1×10^{-5} volts, to bring the absolute values into
agreement with those of the other set. The difference in absolute

values is doubtless due to a parasitic e.m.f. in parts of the circuit beyond the reversing switch, due to different temperature conditions in the room during the two sets of readings, and is evidently without significance, since the quantity in which we are interested here is the variation of e.m.f. with direction in the crystal. The deviations from linearity of the two sets of 16 lay on the same straight line without correction, as should be the case if the difference in e_0 is due to parasitic effects as suggested.

It will be seen from the figures that e_0 and Δ are both linear functions of $\cos^2\theta$; that is, the relation of Kelvin is satisfied for zinc. The results contained in the figures may be used to give the following formulas:

$(\text{t.e.m.f.})_{\text{Zn}_{11}-\text{Cu}}$

$$= 1.372 \times 10^{-6} \times (\tau - 293.1) + 3.03 \times 10^{-10} \times (\tau - 293.1)^2 \text{ Volts};$$

$(\text{t.e.m.f.})_{\text{Zn}_{\perp}-\text{Cu}}$

$$= -0.428 \times 10^{-6} \times (\tau - 293.1) - 3.97 \times 10^{-9} \times (\tau - 293.1)^2.$$

Whence:

$(\text{t.e.m.f.})_{\text{Zn}_{11}-\text{Zn}_{\perp}}$

$$= 1.800 \times 10^{-6} \times (\tau - 293.1) + 4.27 \times 10^{-9} \times (\tau - 293.1)^2,$$

and since

$$P = \tau \frac{dE}{d\tau} \quad \text{and} \quad \sigma = \tau \frac{d^2E}{d\tau^2},$$

we have for the Peltier and Thomson heats:

$$P_{\text{Zn}_{11}-\text{Zn}_{\perp}} = \tau \times [1.800 \times 10^{-6} + 8.54 \times 10^{-9} \times (\tau - 293.1)],$$

$$\sigma_{\text{Zn}_{11}-\text{Zn}_{\perp}} = \tau \times 8.54 \times 10^{-9}.$$

The designation Zn_{11} means that the crystal axis (of six-fold symmetry) is parallel to the length of the rod. The sign convention is the usual one. If $(\text{t.e.m.f.})_{\text{Zn}_{11}-\text{Zn}_{\perp}}$ is positive, current flows from Zn_{11} to $\text{Zn}_{\perp}$ at the hot junction.

It is probable that within the limits of error the relation between temperature and e.m.f. is not quite represented by a second degree expression in the temperature, but the curves of deviation from linearity are systematically unsymmetrical, in that the deviation at

$\frac{3}{4}$ of the temperature range (71°) is slightly greater than at the $\frac{1}{4}$ temperature (37°). The difference is of the order of 4×10^{-7} volts. It is in such a direction as to decrease the curvature at the lower temperature and increase it at the higher temperature end of the range; this means that σ increases with rising temperature somewhat more rapidly than proportionally to the absolute temperature, as given by the formula. In order to make partial allowance for this slight departure from symmetry, the deviation, Δ, at the mean temperature was calculated by taking 0.4 of the sum of the deviations at the $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$ points, this being the fraction to be used if the deviation is accurately parabolic. An idea of the smoothness of the readings, and so of the accuracy, is given by the fact that the actual Δ at the $\frac{1}{2}$ point usually differed from the calculated Δ by only 0.1 or 0.2 mm. deflection of the galvanometer, corresponding to from 4 to 8×10^{-8} Volts.

Compared with my previous measurements,[7] these new results show very important differences. The previous results were obtained with 8 rods, with a maximum angle between basal plane and length of 55°. The results indicated by the previous measurements were that P is not linear against $\cos^2 \theta$ (or against the specific resistance, which is the same thing), but that σ (or Δ) is linear. These new and greatly improved results do not substantiate this conclusion, but both P and σ are linear within satisfactory limits of error. The values given in the previous paper for Peltier heat and Thomson heat of Zn_{11} against Cu were obtained by an extrapolation to nearly double the range of measurement, and cannot, therefore, be expected to be accurate. It follows that the difference between the P and the σ for parallel and perpendicular directions in the former paper (p. 132) cannot be accurate. In fact, the former paper gives for $P_{11-\perp}$ at 0°, $1.001 \times 10^{-6} \times \tau$ against $1.629 \times 10^{-6} \times \tau$ found here; and for $\sigma_{11-\perp}$, $6.2 \times 10^{-9} \times \tau$ against $8.5 \times 10^{-9} \times \tau$ found now. The previous value for the basal plane parallel to the length avoids error from the long range extrapolation, but here there is another source of error in that the copper was not from the same source in the two sets of experiments. In fact the previous measurements give for $P_{Zn\perp-Cu}$ at 0° the value $-.147 \times 10^{-6} \times \tau$, whereas the present value is $-.269 \times 10^{-6} \times \tau$. The difference, which amounts to about a tenth of a micro-volt per degree, does not seem too large for the thermal e.m.f. between two different varieties of commercial copper.

The conclusion that thermal e.m.f. satisfies Kelvin's law agrees with the conclusion reached by Linder[2] from his measurements up to 200°. Linder was of the opinion, however, that at 300° and 400° his departures from the relation were greater than experimental error. It seems to me, however, that this effect of Linder's might well be due to the very steep temperature gradient at the junction, which would make difficult the exact determination of the temperature, and which would have an increasing effect at high temperatures.

After the completion of the thermo-electric measurements, I made new measurements of specific resistance. There were several reasons for doing this. I desired to submit the $\cos^2$ law of Kelvin for resistance to a more accurate check than had yet been made; my previous measurements had been made on only eight samples scattered over a range of orientation of 60° instead of the whole 90°, and there were rather serious differences between the values of Grüneisen and Goens[3] and of myself for the ratio of the resistance parallel and perpendicular to the axis, Grüneisen and Goens finding the ratio 1.080 against my 1.036. At first, on repeating the measurements, disturbingly irregular results were obtained. After considerable work, the source of the irregularities was found in the very great sensitiveness of resistance to slight mechanical deformations. If the rod is slightly bent in removing from the glass mold, or if it sticks to the glass so that deformations are produced by unequal thermal expansion between the mold and metal on cooling, the resistance is materially increased. The reason that this source of error had not been more disturbing in the previous measurements was that the larger diameter of the rods, 6 mm. against 3mm. used here, made deformation incidental to cracking away the glass mold much less likely. It is perhaps surprising that thermal e.m.f. should be much less sensitive to deformation than resistance; this was proved not only by the much greater regularity of the results for thermal e.m.f., which were obtained on rods which must have suffered some deformation, but also by special tests, in which the rods were deliberately bent and straightened, with no measurable change in thermal e.m.f.

It finally proved impossible to obtain measurements of the resistance which were sufficiently regular on rods which had been removed from the molds, and accordingly the resistance was measured before removing the glass. This was done as follows. The potentiometer method of measuring resistance was used. Current

terminals were attached by soldering copper leads to the two ends of the rod, the glass being broken away a sufficient distance to make this possible. The potential terminals were two needles, mounted on a frame at a fixed distance apart, and pressed by springs into contact with the metal through two V-shaped notches ground through the glass wall of the mold with a fine glass-cutting wheel dressed to a sharp edge with a diamond. The notches were ground to such a depth as to just break through the glass. In this way, the only appreciable deformation was confined to the ends near the current terminals, and so was without effect in the region between the potential terminals, which determines the resistance. The angle of the basal plane with the length was determined after the measurements by cooling in liquid air, and by cleavage, as before. The diameter was measured with a micrometer after the glass mold was broken away; the fluctuations from uniformity of diameter in the space between the potential terminals was of the order of 1%.

The specific resistances at 20° of two sets of rods, obtained with all these precautions, are shown in Figure 7 plotted against $\cos^2\theta$. Except for one bad point, the results are fairly regular. In selecting from these data the most probable values for the specific resistance, I assumed that almost all sources of error would give too high a resistance, and that therefore the lowest of the values found are most probably correct. Figure 7 shows that within experimental error specific resistance is linear against $\cos^2\theta$, so that the relation of Kelvin is satisfied. In fact there has never, as far as I know, been any reason to think that Kelvin's relation for resistance might not be correct.

In Figure 7 are also shown my previous values for resistance parallel and perpendicular to the axis. These both differ by a small and nearly constant amount from the value now found. The new value for the ratio of the two resistances is 1.039 (6.06/5.83) against 1.036 found before by extrapolation over a range of 30°. The absolute difference between my former and present results is perhaps to be explained by greater purity in my new supply of zinc; the fact that the difference is constant over the entire range of orientation is against the supposition that the previous high values were due to deformation. Plotted in the same diagram are also the values of Grüneisen and Goens. Their value for the resistance when the axis is perpendicular to the length is almost exactly the same as my new value, but their value for the parallel orientation is much higher.

It seems to be unquestionable that their large value is an effect of distortion, for it is of course true that a crystal is very deformable when the axis is parallel to the length, but comparatively rigid when perpendicular.
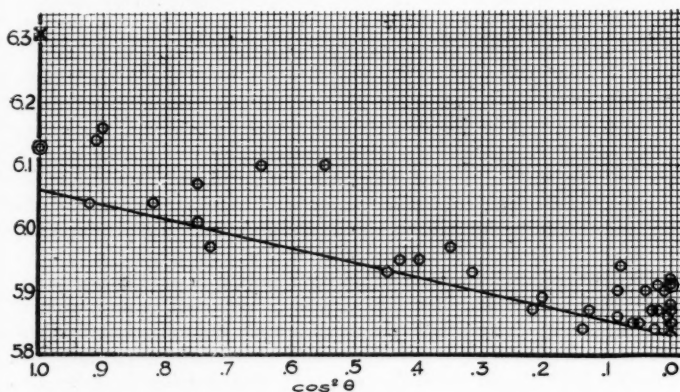

FIGURE 7.   Specific resistance at 20° C in 10^{-6} ohms per cm. cube of single crystal zinc plotted against the square of the cosine of the angle between the crystal axis and the length of the rod.   The double circles are my previous values and the crosses those of Grüneisen and Goens.

Cadmium.   The material was Kahlbaum's best.   At first the attempt was made to fill the molds by suction, drawing the melted Cd up from an open crucible, but this failed because of the unexpectedly rapid oxidation of the molten Cd, even at temperatures close to the melting point.   The oxidation was sometimes so rapid that the coating of brown oxide spontaneously became red hot. The difficulty was not avoided by filling the furnace as completely as possible with a stream of CO_2, led in at the bottom and flowing out at the open upper end.   The rapidity of oxidation seems to increase very markedly as the last traces of impurity are removed from the metal; the purest Cd of American make which I could obtain oxidized very much more slowly.   The filling of the mold was finally accomplished by running the molten metal down from a sealed reservoir attached to the upper end of one of the branches. The two-branch mold with 12 sections was used.   It was exhausted and flushed several times with CO_2 before filling.

Cd is perhaps the most difficult of the metals worked with here to compel to crystallize as one grain, the tendency to switch from one grain to another in the middle of a straight arm being particularly strong. The general behavior is consistent with the explanation that fresh nuclei of the solid are particularly likely to form from the liquid if it is subcooled by a small amount. The remedy is to make the temperature gradient unusually steep in the region where crystallization takes place, in this way reducing to a minimum the extent of the region in which there is any possible subcooling. A steep gradient in the desired locality was produced by lowering the mold into oil, and by various manipulations of the position of the surface of the oil and the temperature of the furnace, which can be learned only by trial. In general, the temperature of the furnace should be further above the melting point than is necessary for other metals.

The determination of the angle between the crystal axis and the length offered some difficulty. Cadmium does not cleave, even at liquid air temperature, and the small size of the rods made difficult the method previously used of marking the reflection pattern on a wooden ball slipped over the rod. At first I tried to determine the orientation by means of the specific resistance, but these results were very irregular, cadmium being even more deformable than zinc, and particularly difficult to prevent from sticking to the glass mold. After various unsuccessful attempts, including an attempt by locating the slip planes when stressed beyond the elastic limit, I returned to the optical method, not attempting, however, to locate the entire reflection pattern, but only the basal plane. A simple arrangement was made for this purpose, in which the crystal rod was mounted in a goniometer holder on an optical bench in a beam of parallel light from an electric arc, and the angle of reflection determined by sighting through two small peep holes. The error may easily be made less than 1° with very simply constructed apparatus. The difficulty with the method is in being sure that the plane of reflection is actually the basal plane. If the basal plane is approximately parallel to the length of the rod, the reflection from it is so much stronger than the reflection from any other plane that there is seldom any trouble. But if the basal plane is inclined at a high angle, then the reflection from it may be weaker than from one of the secondary planes more nearly parallel to the length, and in such a case, decision must be made with the help of other data. There

are never more than a few discrete possibilities to choose between, and a knowledge of the specific resistance, or thermal e.m.f., or perhaps the slip pattern makes possible an unambiguous choice.

Measurements of thermal e.m.f. were made on 64 different samples, four sets of 16 each. This comparatively large number was used because the first measurements, in which the angle was determined from the specific resistance, had indicated a systematic departure from Kelvin's cos²θ law, and if this were really the case, I was anxious to settle it as certainly as possible. The suspected departure did not substantiate itself, however, on increasing the number of readings and determining the orientation in the better way.

The method by which the results were calculated for cadmium differed somewhat from that outlined above. The temperatures of the four sets of runs were so nearly alike that a very small correction sufficed to reduce the readings of any one set to a mean and standard set of temperatures: 20°, 37.20°, 54.03°, 72.00° and 88.14°. Four different plots of the thermal e.m.f.'s of all of the 64 rods between 20° and each of the other temperatures were then made against cos²θ. In each case the points so obtained lay on a straight line, confirming Kelvin's law. The observed points for the interval 20°–88.14° are reproduced in Figure 8. Kelvin's law having thus been established, it remained only to get the best e.m.f.'s for the parallel and the perpendicular orientations; these were found from the intercepts of the best straight lines drawn through the experimental points. Next, the best second degree curve in the temperature was passed through these intercepts. In this way the following results were found:

$(\text{t.e.m.f.})_{\text{Cd}_{11} - \text{Cu}}$

$$= (1.357 \times 10^{-6})(\tau - 293.1) - 0.790 \times 10^{-8}(\tau - 293.1)^2 \text{ Volts,}$$

$(\text{t.e.m.f.})_{\text{Cd}_{\perp} - \text{Cu}}$

$$= - (1.616 \times 10^{-6})(\tau - 293.1) - 1.872 \times 10^{-8}(\tau - 293.1)^2.$$

Whence:

$(\text{t.e.m.f.})_{\text{Cd}_{11} - \text{Cd}_{\perp}}$

$$= (2.973 \times 10^{-6})(\tau - 293.1) + 1.082 \times 10^{-8}(\tau - 293.1)^2,$$

and for the Peltier and Thomson heats:

$$P_{\text{Cd}_{11} - \text{Cd}_{\perp}} = \tau \times [2.973 \times 10^{-6} + 2.164 \times 10^{-8}(\tau - 293.1)],$$

$$\sigma_{\text{Cd}_{11} - \text{Cd}_{\perp}} = \tau \times 2.164 \times 10^{-8}.$$
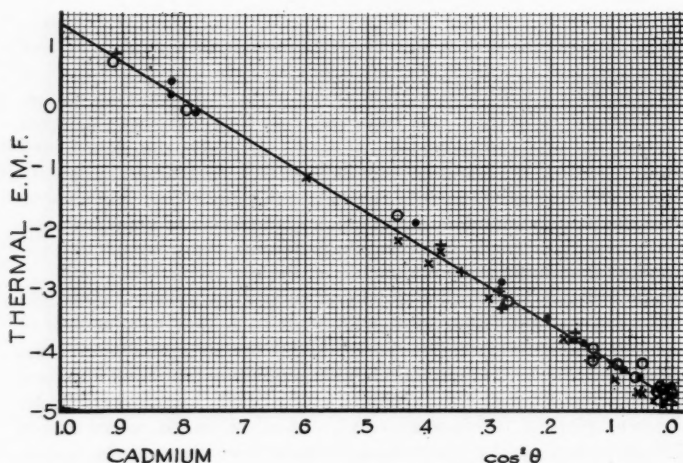
FIGURE 8. Thermal e.m.f. of single crystal cadmium against copper between 20° and 88.14° C. The ordinates are on an arbitrary scale, one large division corresponding to 40.15×10^{-6} volts. The abscissas are the squares of the cosine of the angle between the crystal axis and the length. The different designations of the observed points refer to different set-ups of the apparatus.

As in the case of zinc, the second degree curve does not quite reproduce the measurements, but there are small differences which are probably larger than experimental error. At the three temperatures 37.2°, 54.0°, and 72.0° the actual $(t.e.m.f.)_{Cd_{11}-Cu}$ is to be found by adding to the values given by the second degree formula -0.2×10^{-6}, $+0.2 \times 10^{-6}$, and $+0.1 \times 10^{-6}$ Volts, respectively, and similarly, to obtain the actual $(t.e.m.f.)_{Cd_{\perp}-Cu}$ the above formula is to be corrected by -0.4×10^{-6}, -0.6×10^{-6}, and $+0.9 \times 10^{-6}$ Volts, respectively. The correction term has the effect of decreasing the curvature, and therefore σ, at the low temperature end, and increasing it at the high temperature end.

We now compare these new results with those previously found. The previous values were obtained with 14 rods, distributed over practically the entire orientation range. Because the previous results were obtained without extrapolation, better agreement is to

be expected than in the case of zinc. There is, however, the uncertainty in the previous results that the orientation was determined in terms of the specific resistance, which we have just seen does not give regular results.

The previous results agree with the new ones in that Kelvin's relation was found to hold. At $0°$ C the previous values for $P_{Cd_{11}-Cd_{\perp}}$ was $+ 2.95 \times 10^{-6} \times \tau$ against $+ 2.54 \times 10^{-6} \times \tau$ now found, and for $\sigma_{Cd_{11}-Cd_{\perp}}$, $+ 1.7 \times 10^{-8} \times \tau$ against $+ 2.2 \times 10^{-8} \times \tau$ now found.

Of the many sets of castings, only one was perfectly satisfactory for the determination of specific resistance, all the others sticking slightly to the glass or else having been partially deformed. Readings were made on this set before removing the glass mold, connections to the potential terminals being through notches ground in the glass, as in the case of zinc. The results are shown in Figure 9. It is evident that the $\cos^2$ law is satisfied within experimental error. My previous values are shown as double circles in the figure; these agree rather closely with the new values. I believe that a study of the data will suggest that the new value for the resistance when the basal plane is perpendicular to the length, 8.24, is somewhat preferable to the former value 8.30, in spite of the fact that the distribution of orientations in the previous work was somewhat wider. The values of Grüneisen and Goens[8] are also shown in the figure. These are higher than my values at both orientations by such an amount that their ratio of the resistances (8.45/7.11 = 1.188) does not differ by much from mine (8.24/6.82 = 1.207). The difference between my results and those of Grüneisen and Goens is in the direction to be explained by impurity or deformation in their material.

Antimony. The material was Kahlbaum's; I have not been able to obtain antimony from any other source of sufficient purity. The molds in which the single crystal rods were cast were made of quartz tubing; it would have been possible to use glass combustion tubing, but the softening point of this glass is so near the melting temperature, and other mechanical difficulties in handling the glass are so great, that the much greater convenience of the quartz much outweighed the greater expense. Fortunately antimony does not stick to quartz (or to glass either) so that it was not necessary to coat the mold, which would have been difficult at temperatures above a red heat. The first batch of castings was made in one of the complicated many-arm molds. The greatest difficulty with antimony
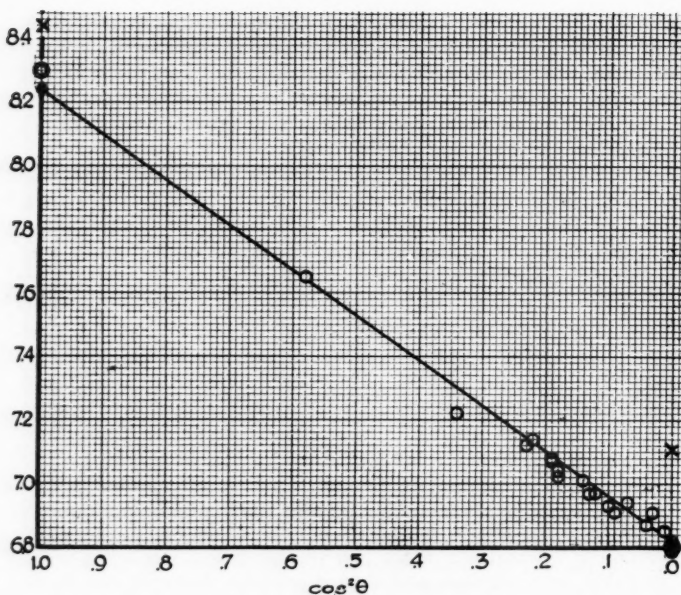
FIGURE 9. The specific resistance in 10^{-6} ohms per cm. cube at $20°$ of single crystal cadmium against the square of the cosine of the angle between the crystal axis and the length. The double circles show my previous values for the extreme orientations, and the crosses the values of Grüneisen and Goens.

is in the appearance of bubbles during filling; many of these appeared in the filling of the many-arm mold, and they could not be eliminated by any means that suggested themselves, so that many of the arms were of no use. I therefore returned to the much simpler mold with only six arms, made by bending a straight piece of quartz tubing at the desired angles. This was filled by slow suction from above, and the tube sealed off. The melted antimony was contained in an open porcelain crucible in the bottom of the furnace, and oxidation was sufficiently prevented by filling the furnace with a stream of CO_2. The advantage of this simple method is that if a bubble of gas appears during the filling, the mold can be allowed to empty

itself and the process repeated until successful. Two of these six-arm molds could be filled at the same time from the same crucible, and thus 12 castings obtained by the same lowering operation. The higher orientations (cleavage perpendicular to the length) are more reluctant to appear with antimony than with most of the other metals, and even when once obtained, manipulation is difficult because of extreme brittleness. It is almost impossible to crack the quartz mold away from a rod with cleavage plane perpendicular to the length without breaking the rod. The method which I finally adopted was to grind the mold away from two sides, holding the quartz tube pressed lengthwise against a flat grinding surface, until the quartz was entirely ground through, as shown in section in Figure 10, when the remains of the mold will drop off.
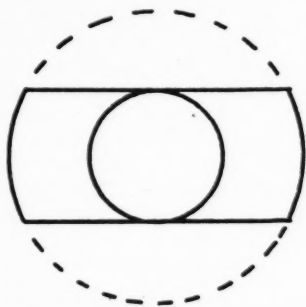

FIGURE 10. Shows the method of grinding away the quartz mold from the single crystals of antimony in order to avoid breaking the crystal when the cleavage plane is very nearly perpendicular to the length.

The orientation was determined with a simple goniometer from the cleavage, made with a knife at room temperature.

Three sets of runs were made to get the thermal e.m.f. The first set was on 12 rods obtained from the complicated many-arm mold. The second set was on 16 rods selected so as to give the widest range of orientation from four batches of castings made in the simple 6-arm molds. None of these rods was of very high orientation. The third set was on two pieces, both from the same original rod, with the cleavage plane at 83° to the length. These pieces were so short that it was not possible to use the regular ar-

rangements; a new bakelite block was therefore made, machined so
as to be only 3 mm. thick at the part where the rods were inserted,
instead of 2.5 cm., and with special stuffing boxes of minimum depth.
These two pieces from the same rod gave identical results, and they
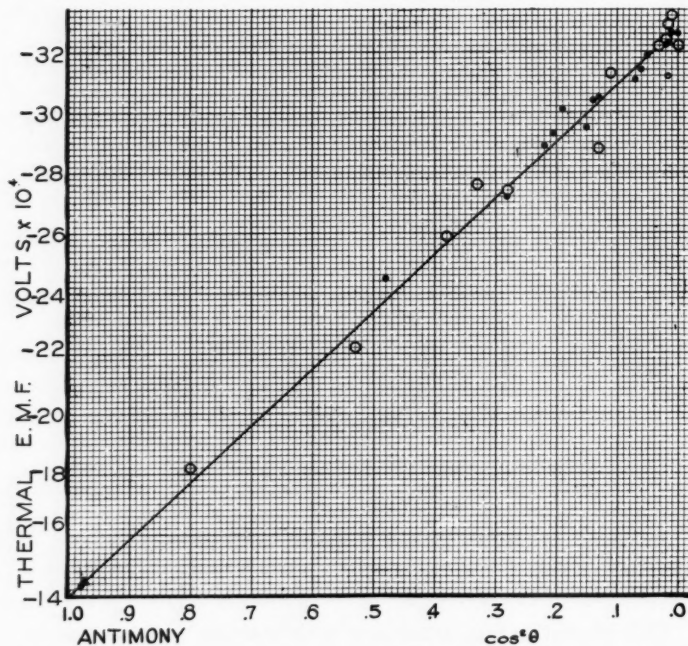are shown in the following figures slightly separated.

FIGURE 11. Thermal e.m.f. between 20° and 88° C in 10^{-4} volts of single
crystal antimony against copper as a function of the square of the cosine
of the angle between the crystal axis and the length.

The results for antimony were not as regular as for the other
metals; doubtless the reason is connected with the short length of
the specimens, so that irregular temperature fluctuations, due to
greater proximity of the walls, were more important. The results
for thermal e.m.f. between 20° and 88° are shown in Figure 11 for

all specimens, and in Figure 12 for the deviation from linearity at
the mean temperature. It is seen that within the limits of experi-
mental error there is no reason to suspect a departure from Kelvin's
cos² law. The great scattering of the points for the deviation from
linearity shows that there is considerable error in the curvature
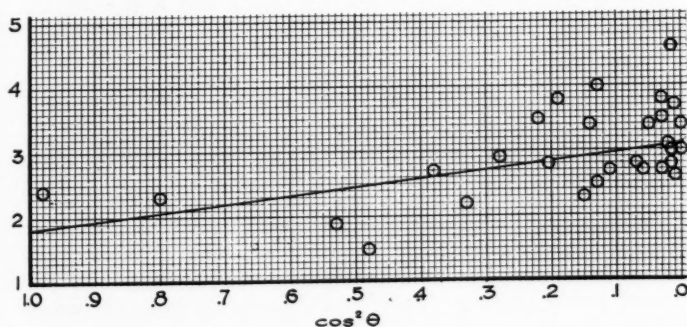deduced from these results.

FIGURE 12. The deviation from linearity in the relation between tem-
perature and thermal e.m.f. of single crystal antimony against copper. The
deviation is shown in 10^{-5} volts at the mean temperature 54°, the tempera-
ture range being from 20° to 88° C. The abscissa is the square of the angle
between the crystal axis and the length of the rod.

In spite of this comparatively large uncertainty, it is again prob-
able that a second degree series in the temperature does not suffi-
ciently reproduce the results. The departure from linearity was not
quite symmetrical about the mean, the deviation being greater on
the higher temperature side, so that the actual curvature is less at
the lower temperature end and greater at the high temperature end
than given by the second degree expression. The dissymmetry is
of the order of 10^{-5} Volts, or $\frac{1}{2}\%$ of the maximum t.e.m.f. I do
not believe that the data justify an attempt to make a more precise
statement about a possible departure from the second degree re-
lation.

Expressing the results in the form of the best second degree series,
the following values were found:

$(t.e.m.f.)_{Sb_{11}-Cu}$

$$= -19.5 \times 10^{-6} \times (\tau - 293.1) - 1.55 \times 10^{-8} \times (\tau - 293.1)^2 \text{ Volts},$$

$(t.e.m.f.)_{Sb_\perp - Cu}$

$$= -46.2 \times 10^{-6} \times (\tau - 293.1) - 2.66 \times 10^{-8} \times (\tau - 293.1)^2.$$

Whence:

$(t.e.m.f.)_{Sb_{11} - Sb_\perp}$

$$= +26.7 \times 10^{-6} \times (\tau - 293.1) + 1.11 \times 10^{-8} \times (\tau - 293.1)^2,$$

and

$$P_{Sb_{11} - Sb_\perp} = \tau \times [26.7 \times 10^{-6} + 2.22 \times 10^{-8} \times (\tau - 293.1)],$$

$$\sigma_{Sb_{11} - Sb_\perp} = \tau \times 2.22 \times 10^{-8}.$$

In the previous paper I was able to measure the t.e.m.f. of only one sample of antimony, with the cleavage plane parallel to the length. For this I found:

$(t.e.m.f.)_{Sb_\perp - Cu}$

$$= -61.6 \times 10^{-6} \times (\tau - 293.1) - 8.5 \times 10^{-8} \times (\tau - 293.1)^2.$$

This former value is without doubt much too high; the reason for it is not evident.

The value of the Peltier heat between Sb_{11} and $Sb_\perp$ is so large as to have a special significance that must be emphasized. At 20° C the formula above gives for $P_{Sb_{11} - Sb_\perp}$ the value $293 \times 26.7 \times 10^{-6}$ = 0.0078 Volts. This means that 1 coulomb absorbs 0.0078 joules ($= 7.8 \times 10^4$ ergs) in flowing from the parallel to the perpendicular direction. The amount absorbed by one electron is therefore $-1.59 \times 10^{-19} \times 7.8 \times 10^4 = -1.24 \times 10^{-14}$ ergs. Now the energy of a gas molecule at 20° C is 6.05×10^{-14} ergs, so that in antimony one electron, in flowing from a direction of motion perpendicular to one parallel to the axis of the crystal, absorbs *as heat* 0.2 of the classical equipartition energy. It will be seen later that the corresponding quantity for bismuth is about twice as great. This is evidently a most important point for any theory of conduction. It would seem to indicate that the thermal energy of the conduction electrons must be of the same order of magnitude as given by classical equipartition. It is not obvious what account would be given of this situation by such a theory as that of Sommerfeld,[8] in which the part of the energy of the electrons which varies with temperature is supposed to be much less than the classical amount.

The determination of the specific resistance of this new material

was a comparatively straightforward matter, the danger of deformation being very small because of its brittleness. The results are shown in Figure 13. Again the cos² law is satisfied within experimental error. My previous values are also shown in the figure; these were obtained from only four specimens, with the cleavage plane at 0°, 0°, 47°, and 66° to the length respectively. It is not surprising that the agreement is not better. It is to be noted that the abnormal result previously found is sustained, namely that the
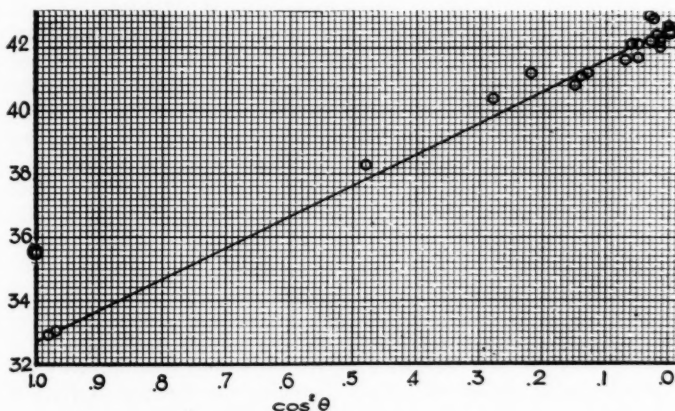

FIGURE 13. The specific resistance in 10^{-6} ohms per cm. cube at $20°$ C of single crystal antimony as a function of the square of the cosine of the angle between the crystal axis and the length. My previous values for the extreme orientations are shown by the double circles. The best values seem to be: 32.7×10^{-6} for the cleavage plane perpendicular to the length, and 42.6 for the parallel orientation.

resistance across the cleavage plane is less than parallel to the plane; in all other metals the behavior is the reverse. The discrepancy between my previous results and the new one for cleavage plane perpendicular to the length is in the direction to be accounted for by minute fissures on the cleavage plane in the former sample.

   The Pressure Coefficient of Resistance of Single Crystal Antimony. Advantage was taken of the greater range of orientation of the specimens now available to extend my previous measurements[9] of the

effect of pressure on resistance. The previous measurements were made on two samples with the cleavage plane at 0° and 47.5° to the length. The new measurements were made on three specimens, with the cleavage plane at 7°, 42.5°, and 83° to the length. Measurements were made in the routine manner with the potentiometer. Current and potential leads were both soldered to the specimen, using very fine leads and a minimum amount of solder for the potential leads. Measurements were made at 30° and 75°, thus incidentally giving values for the temperature coefficient of resistance. The transmitting medium was petroleum-ether. In this way the irregular effects with the samples with high orientations previously found were completely avoided; these effects were ascribed to minute fissures produced by the viscosity under pressure of the transmitting medium. The regularity of the new results is shown by the following values for the average departure of a single reading from a smooth curve, in terms of percentage of the maximum pressure effect, at 30° and 75° respectively for the three orientations in the order given above: 0.50%, 4.0%; 0.18%, 0.22%; 0.08%, 0.17%. The larger error for the cleavage plane parallel to the length is explained by the much smaller value of the pressure coefficient in this direction.

The change of resistance produced by pressure cannot be represented within experimental error by any simple expression. For the 83° and the 42.5° orientations, the deviations from linearity are unsymmetrical about the mean pressure, the greatest deviations occurring at pressures less than the mean. The asymmetry is more pronounced for the 42.5° orientation. For the 7° orientation, the deviation from linearity reverses sign, being negative for low pressures and positive for high pressures; this effect is the more marked at the low temperature. In view of all these complications, the results are not indicated by a formula, but by a table (Table I), giving the resistance at 1000 kg intervals of pressure at 30° and 75°. In making the calculations, the relative resistance of each sample was first expressed in terms of its resistance at atmospheric pressure and 30° C as unity. These numbers were then multiplied by the specific resistance at 30° and atmospheric pressure to give the figures in the table. The specific resistance at 30° and atmospheric pressure was obtained from Figure 13, using in passing from 20° to 30° the values of the mean temperature coefficient shown in Table I. This mean temperature coefficient was obtained by linear extrapolation

of the resistance measured at 30° and 75° during the pressure runs.
The resistance of antimony is not linear with temperature, so that
extrapolation is not quite correct, but it can only be a very little
in error, because the range of temperature of the measurement,
30°–75°, is so nearly in the middle of the range 0°–100°.

The resistances listed in Table I are thus nearly specific resist-
ances; they are, however, not quite this, because the resistances
under pressure were obtained with terminals fixed to the specimen.
To get specific resistances from these measurements, a correction
must be applied for the distortion under pressure.   From the elastic
constants which I have previously determined it may be easily
computed that when the basal plane is parallel to the length, the
measured resistance at 10,000 kg must be corrected by subtracting
1.69% to convert to specific resistance, and when the basal plane
is perpendicular to the length, the correction is an addition of 0.68%.
These figures are also approximately the figures for the 7° and 83°
directions respectively given in the table.

TABLE I.

RESISTANCE OF ANTIMONY.

Pressure kg. /cm.³	Resistance × 10⁶					
	Basal Plane at 7° to length		Basal Plane at 42°.5 to length		Basal Plane at 83° to length	
	30° C	75° C	30° C	75° C	30° C	75° C
0	44.41	53.37	40.01	48.81	34.60	42.47
1000	44.58	53.38	40.30	49.09	35.22	43.21
2000	44.76	53.40	40.66	49.43	35.95	43.94
3000	44.93	53.43	41.06	49.72	37.05	44.89
4000	45.11	53.51	41.52	50.09	37.78	45.94
5000	45.28	53.56	42.00	50.48	38.61	46.83
6000	45.45	53.65	42.49	50.89	39.60	47.86
7000	45.63	53.74	43.01	51.30	40.63	48.92
8000	45.80	53.78	43.53	51.73	41.70	50.02
9000	45.98	53.81	44.05	52.16	42.80	51.16
10000	46.16	53.82	44.58	52.59	43.93	52.32
11000	46.33	53.82	45.13	53.03	45.07	53.48
12000	46.50	53.78	45.66	53.38	46.20	54.60
Mean Temp. Coefficient, 0°–100°	.00495		.00551		.00572	

Comparing these new results with the previous values, the most important qualitative features found before are verified, but the numerical agreement is not very close. For the 7° direction, the minimum of resistance with increasing pressure is found again. As before, this minimum of resistance occurs first at higher temperatures. The pressure coefficient perpendicular to the basal plane is, as before, found to be very much greater than parallel to the plane. The difference is so great that at some pressure not very far beyond the maximum of 12,000 the initial abnormality of a resistance greater parallel than across the cleavage plane will be wiped out. Previously the disappearance of the abnormality was found actually to take place within the experimental range of pressure.

Tin. Kahlbaum's tin was used. Two sets of measurements of thermal e.m.f. were made, on two sets of 16 rods, selected from two different castings in the complicated mold with many branches. The orientation of these small rods was not easy to determine. Tin has no cleavage and the basal plane is absent from the reflection pattern, so that to determine the orientation from the reflection pattern would have demanded the location of several of the other planes, and not enough of these were usually present to make this possible. Accordingly I had to be satisfied with a measurement of specific resistance to give the orientation. Fortunately, tin is not as deformable as zinc or cadmium, and furthermore its resistance is comparatively insensitive to deformation, as was shown by direct trial, and also by the fact that the measurements of thermal e.m.f. were very much more regular when plotted against resistance than had been the case with zinc or cadmium.

In Figure 14 is plotted the total e.m.f. against copper between 20° and 87.8° as a function of the specific resistance at 20°. The readings of one set have been corrected by a small constant amount to make their mean agree with the other set; the difference between the two sets is doubtless due to different parasitic e.m.f.'s during the two runs, as has already been explained in connection with zinc. Within experimental error, thermal e.m.f. could be represented by a second degree series in the temperature. The deviations of the observed points from linearity at the mean temperature are shown in Figure 15. It is evident that within error the deviation is a linear function of the specific resistance, as is demanded by Kelvin's law. The total e.m.f., on the other hand, seems to be very definitely not a linear function. To a sufficient degree of approximation, the
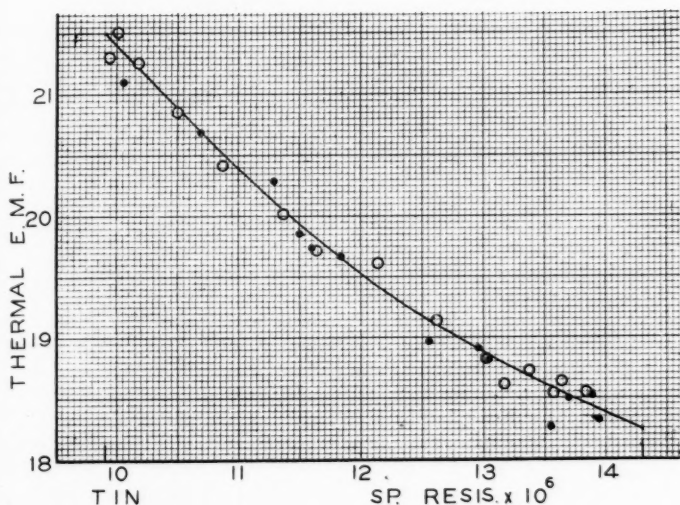
FIGURE 14. Thermal e.m.f. between 20° and 87.8° of single crystal tin against copper as a function of the specific resistance of the tin at 20°. The ordinates are centimeters deflection of the galvanometer; one centimeter is the equivalent of 1.096×10^{-5} volts.

e.m.f. is a second degree function in $\cos^2\theta$, so that the results can be reproduced by describing the behavior at the 0°, 45°, and 90° orientations. The results are as follows:

$(t.e.m.f.)_{Sn_{11}-Cu}$

$$= (2.650 \times 10^{-6}) \times (\tau - 293.1) + 4.29 \times 10^{-9} \times (\tau - 293.1)^2 \text{ Volts,}$$

$(t.e.m.f.)_{Sn_{45}-Cu}$

$$= (2.909 \times 10^{-6}) \times (\tau - 293.1) + 3.44 \times 10^{-9} \times (\tau - 293.1)^2,$$

$(t.e.m.f.)_{Sn_\perp-Cu}$

$$= (3.307 \times 10^{-6}) \times (\tau - 293.1) + 2.47 \times 10^{-9} \times (\tau - 293.1)^2,$$

$(t.e.m.f.)_{Sn_{11}-Sn_{45}}$

$$= (-.259 \times 10^{-6}) \times (\tau - 293.1) + 0.85 \times 10^{-9} \times (\tau - 293.1)^2,$$
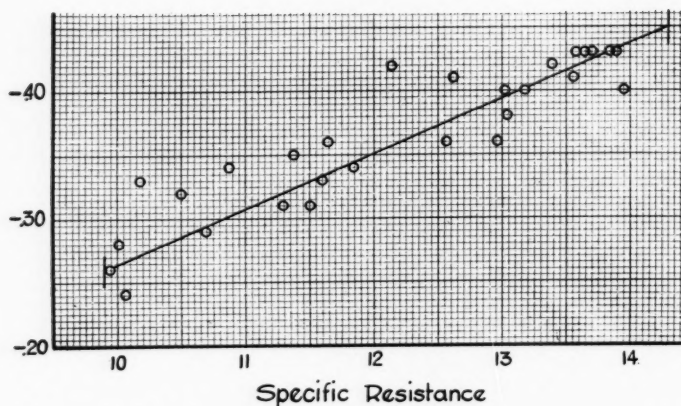
FIGURE 15.   The deviation from linearity in the relation between temperature and thermal e.m.f. of single crystal tin against copper.   The deviation is shown in terms of centimeters deflection of the galvanometer (1 cm. = 1.096×10^{-5} volts) at the mean temperature 53.9°, the temperature range being from 20° to 87.8° C.   The abscissa is the specific resistance at 20° $\times$ 10^6.

$(\text{t.e.m.f.})_{\text{Sn}_{11}-\text{Sn}_\perp}$

$$= (-.657 \times 10^{-6}) \times (\tau - 293.1) + 1.82 \times 10^{-9} \times (\tau - 293.1)^2,$$

$$P_{\text{Sn}_{11}-\text{Sn}_{45}} = \tau \times [-.259 \times 10^{-6} + 1.70 \times 10^{-9} \times (\tau - 293.1)],$$

$$\sigma_{\text{Sn}_{11}-\text{Sn}_{45}} = \tau \times 1.70 \times 10^{-9},$$

$$P_{\text{Sn}_{11}-\text{Sn}_\perp} = \tau \times [-.657 \times 10^{-6} + 3.64 \times 10^{-9} \times (\tau - 293.1)],$$

$$\sigma_{\text{Sn}_{11}-\text{Sn}_\perp} = \tau \times 3.64 \times 10^{-9}.$$

The previous results* for tin were obtained from 14 specimens, of which only one had the basal plane approximately perpendicular to the length, the 13 others having the angle less than 40°; the results, furthermore, were much more scattering than the present ones, so that there is no doubt that the new results are much to be preferred.   The value formerly found for the Peltier heat at 0° C

* In the previous paper,[1] the signs of the Peltier heat for tin given in Table II on page 132 should be negative instead of positive.

from the parallel to the perpendicular direction was $\tau \times (-.75 \times 10^{-6})$ against $\tau \times (-.73 \times 10^{-6})$ found here. The goodness of the agreement must be in part fortuitous. The previous measurements showed no difference in the Thomson heat between the perpendicular and the parallel directions; the difference found here is small. The e.m.f.'s against copper previously found were about 0.20×10^{-6} Volts lower than the new values; the difference is doubtless due to difference in the quality of the copper.

There are, of course, no measurements of the resistance as a function of the orientation, as there were for the other metals, since the method of determining the orientation did not permit this.

Bismuth. The material was Kahlbaum's. A large number of castings were made in the complicated many-arm molds. The orientation was determined from the cleavage plane; in a few cases the cleavage was made at liquid air temperatures, but cleavage at room temperature of rods as small as these was so easy that this refinement was not necessary. Four sets of measurements of thermal e.m.f. were made from four sets of 16 rods, selected to cover the orientation range.

Within experimental error the relation between e.m.f. and temperature is of the second degree in the temperature. In Figure 16 is shown the total e.m.f. between 20° and 88° against copper of the 64 specimens, plotted against $\cos^2\theta$, and in Figure 17 the deviations from linearity at the mid temperature. As in the case of tin, the total e.m.f. seems to definitely depart from Kelvin's $\cos^2$ law. The departure is not large, and the results can be sufficiently reproduced by giving the formulas for the 0°, 45°, and 90° orientations. The results follow:

$(\text{t.e.m.f.})_{\text{Bi}_{11}-\text{Cu}}$

$$= 1.084 \times 10^{-4} \times (\tau - 293.1) - 7.27 \times 10^{-8} \times (\tau - 293.1)^2 \text{ Volts,}$$

$(\text{t.e.m.f.})_{\text{Bi}_{45}-\text{Cu}}$

$$= .868 \times 10^{-4} \times (\tau - 293.1) - 3.46 \times 10^{-8} \times (\tau - 293.1)^2,$$

$(\text{t.e.m.f.})_{\text{Bi}_\perp-\text{Cu}}$

$$= .572 \times 10^{-4} \times (\tau - 293.1) + 0.26 \times 10^{-8} \times (\tau - 293.1)^2.$$

Whence follows:

$(\text{t.e.m.f.})_{\text{Bi}_{11}-\text{Bi}_{45}}$

$$= .216 \times 10^{-4} \times (\tau - 293.1) - 3.81 \times 10^{-8} \times (\tau - 293.1)^2,$$
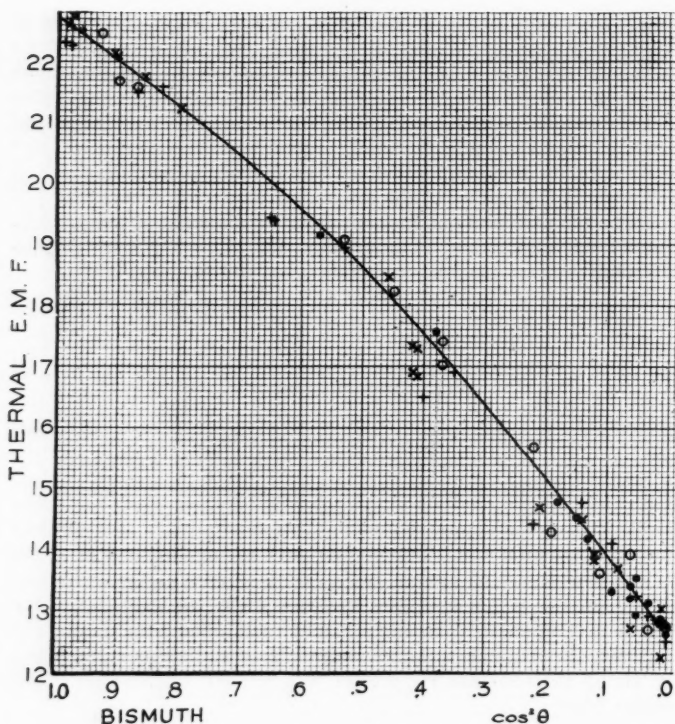
FIGURE 16. Thermal e.m.f. between 20° and 88° of single crystal bismuth against copper as a function of the square of the cosine of the angle between the crystal axis and the length. The ordinates are centimeters deflection of the galvanometer; one centimeter is the equivalent of 3.10×10^{-4} volts. The different symbols on the observed points refer to runs with different set-ups.

$(\text{t.e.m.f.})_{\text{Bi}_{11}-\text{Bi}_{\perp}}$

$$= .512 \times 10^{-4} \times (\tau - 293.1) - 7.53 \times 10^{-8} \times (\tau - 293.1)^2,$$
and:

$$P_{\text{Bi}_{11}-\text{Bi}_{44}} = \tau \times [.216 \times 10^{-4} - 7.62 \times 10^{-8} \times (\tau - 293.1)],$$
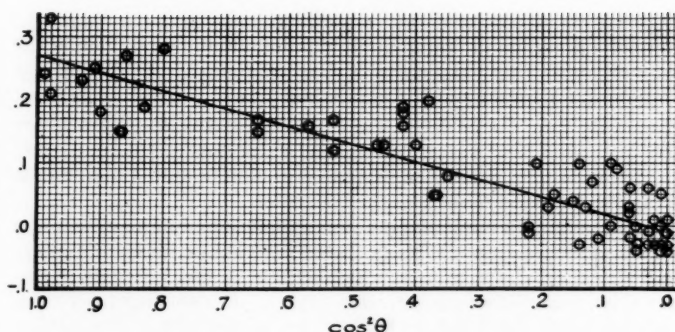
FIGURE 17. The deviation from linearity in the relation between temperature and thermal e.m.f. of single crystal bismuth against copper. The deviation is shown in terms of centimeters deflection of the galvanometer (1 cm.= 3.10 × 10⁻⁴ volts) at the mean temperature 54°, the temperature range being from 20° to 88°. The abscissa is the square of the cosine of the angle between the crystal axis and the length.

$$\sigma_{Bi_{11}-Bi_{45}} = \tau \times [-7.62 \times 10^{-8}],$$

$$P_{Bi_{11}-Bi_{\perp}} = \tau \times [.512 \times 10^{-4} - 15.06 \times 10^{-8} \times (\tau - 293.1)],$$

$$\sigma_{Bi_{11}-Bi_{\perp}} = \tau \times [-15.06 \times 10^{-8}],$$

My previous results for bismuth covered a range of orientation of only 21°, so that a comparison with previous results is profitable only for the perpendicular orientation. The former value for the Peltier heat against copper was 0.578 × 10⁻⁶ × τ at 0° C, against 0.571 × 10⁻⁶ × τ found now. The agreement is good; better agreement is to be expected here than for the other metals because the absolute magnitude of the effects are so much larger for bismuth. Since my previous results were published, Boydston[10] has measured the thermal e.m.f. of single crystal bismuth. He used constantan as the metal of comparison, so that his results are not directly comparable with mine. It may be deduced from his Figure 1 on page 913 of his paper that the thermal e.m.f. between 0° and 100° C of a couple composed of $Bi_{\perp} - Bi_{11}$ is about 5.4×10^{-3} Volts, against 4.7×10^{-3} to be deduced from my formulas above. Boydston's material covered a range of orientation up to within 23° of perpendicularity of basal plane to length, so that no large error is to be

expected in his extrapolation to 90°. A more probable source of error I believe to be impurity in Boydston's bismuth. His metal was obtained from Mallinckrodt, and contained 0.04% of silver. This is not so stated in his paper, but I have learned from correspondence that the omission was due to an oversight. Now I have already found that silver[11] in amount even smaller than this may be responsible for important changes in the properties; I shall return to this question in discussing the resistance.*

In my previous work[9] the specific resistance had been found from a series of measurements on specimens covering an orientation range of only 45°. The points were furthermore rather scattering (Figure 6 on page 531 of my previous paper). In deducing from those measurements the most probable value of resistance, the guiding idea was that the lowest values were most likely to be correct, since high values can easily be produced by slight fissures on the cleavage plane due to deformation. The values deduced for specific resistance at 20° were: $\rho_\perp = 109 \times 10^{-6}$ and $\rho_{11} = 138 \times 10^{-6}$. The ratio of the two resistances was thus only 1.27, against nearly 1.6 reported by practically all early observers.† Adopting a suggestion endorsed

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* The thermo-electric properties of bismuth as a function of orientation have also been measured by Borelius and Lindh,[12] but it is not possible to compare their results with mine because of the very great variations which they find are produced by the temperature history of the specimen. About all that can be said is that their thermal e.m.f. between the two directions is of the same order of magnitude as that found here.

† Grüneisen (Handbuch der Physik, vol. XIII, p. 12) quotes Borelius and Lindh as giving the ratio 1.34, but it is not obvious from what part of their work this figure was obtained. Probably it was deduced from Figure 2 on page 613 of their paper in Ann. Phys. 51, 1916. But Borelius and Lindh were apparently not willing to commit themselves as to just what the ratio of the specific resistances really is, in view of the large effect which they attributed to fissures. Thus on page 614 of the paper just quoted they say: "This survey makes it very probable that the excess resistance (parallel to the axis over that perpendicular to the axis) becomes very small or entirely vanishes under sufficient pressure." In a later paper (Ann. Phys. 53, p. 124, 1917), in describing the symmetry relations of the resistance, they give for the resistance at 20° C, perpendicular, at 45°, and parallel to the axis the figures 1.24, 1.41, and 1.92×10^{-6}, which makes the ratio 1.55, but they remark that the figure 1.92 can be brought down to 1.51 by pressure. The general impression which the work of Borelius and Lindh gives is that in their opinion most, if not all, of the differences observed between different directions in bismuth are due to fissures or internal stresses.

by Borelius and Lindh, I attributed the difference to the effect of fissures.   Since that work, a new determination has been made by Schneider,[6] who finds 1.62 for the ratio; Schneider is apparently inclined to accept my explanation of the discrepancy as due to the effect of fissures.   It seemed therefore important to settle this question as definitely as possible.   I was in a position to much improve on my former results because I could now cover the entire range
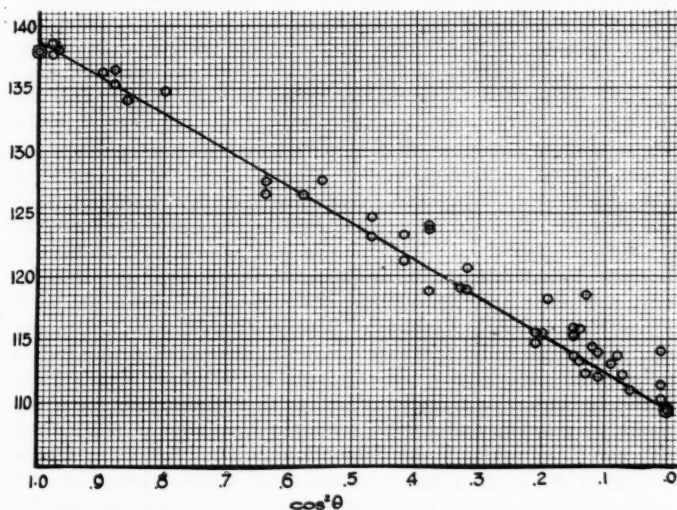

FIGURE 18.   Specific resistance in 10^{-6} ohms per cm. cube at 20° of single crystal bismuth as a function of the square of the cosine of the angle between the crystal axis and the length.

of orientation.   I did not make measurements on the crystals before they had been removed from the glass mold, as had been done for zinc and cadmium, but I selected from the large number of specimens those which had received little or no bending, and which sufficiently covered the entire range of orientation.   All the results for the specific resistance of these selected specimens, *making no discards*, are shown in Figure 18 plotted against $\cos^2\theta$.   It is evident in the first place, that Kelvin's $\cos^2$ law for specific resistance is satisfied.

In the figure are also shown as double circles my previous values for the parallel and perpendicular orientations; it is evident that these values were substantially correct.

Since the experimental work of this paper was done, a paper has appeared by Kapitza (Proc. Roy. Soc. 119, 358, 1928), in which a very careful investigation was made of the resistance as a function of direction. Kapitza grew his crystals by a modified method in which the crystal was not constrained by a mold. He found specimens with abnormally high resistance, but a study of the effect of compression on these led him to accept the explanation that the effect is due to minute cracks. He gives as the best values for resistance: 139×10^{-6} perpendicular to the cleavage plane, and 107 parallel to it. The ratio is 1.30, not far from my value 1.27. I believe that my value is somewhat to be preferred, because Kapitza's values for the parallel orientation showed considerable scattering, from 107 to 114, but in any event there can now be no question whatever that the true ratio cannot possibly be as high as found by the early observers.

I now believe that there are two possible explanations for the large value found for this ratio by other observers; one is the effect of fissures, as already suggested. This is substantiated by my own observations made on specimens in which the bending was known to be severe, which gave points lying very far above the curve of Figure 18 (these points are not shown in the diagram), by the observation of Borelius and Lindh[12] that the resistance of a rod with cleavage plane perpendicular to the length receives a large discontinuous decrease on applying a small longitudinal pressure in such a direction as to close the hypothetical fissures, and now by the recent work of Kapitza. But that this is not the only explanation became obvious on examining some of the specimens of Schneider, which had the high ratio, and which he was so kind as to send. On applying hydrostatic pressure, these showed no discontinuity whatever of resistance, as must have been the case if there had been cracks. I found that the temperature coefficient of resistance of these samples of Schneider was only 0.0032 instead of 0.0044 to be expected for pure bismuth. I have already found that a minute trace of silver has a large effect on temperature coefficient, and Schneider's bismuth is known to contain 0.04% silver. It seems possible that during the slow cooling incident to casting in unicrystalline form the silver may segregate on the basal planes in such a

way as to increase the resistance to flow perpendicular to this plane, but not to affect it very much for parallel flow. Silver is one of the commonest impurities in bismuth, and it is also very difficult to remove, so that the same source of error may have been present in the material of some of the other observers.

On the Rotational Symmetry of Thermal E.M.F.

Altogether, I spent much more time in the investigation of bismuth than of the other metals, since the chance of finding new effects in bismuth is higher because of the larger numerical values to be expected. One of the questions investigated was that of the rotational symmetry of the thermo-electric properties. The symmetry is assumed to be of this sort in the argument of Kelvin, but if Kelvin's $\cos^2$ relation does not hold, as apparently it does not for bismuth, it becomes important to examine this assumption. I briefly touched on this question in my previous paper; I had not realized the importance of the question on gathering the data for that paper, and my argument rested on the general smoothness of the results and two fortuitous measurements for bismuth. I have now made a systematic examination of this question. In one set of 16 rods, not only was the orientation of the cleavage plane with respect to the length determined, but also the orientation of the secondary cleavage planes; these two together are sufficient to completely define the orientation of the rod with respect to the crystal. The secondary cleavage planes were determined from the triangular pattern which close examination will almost always disclose in the basal cleavage plane. Secondary cleavages may be started from the sides of this triangular pattern. The set of rods chosen all had the basal plane nearly parallel to the length, since for this orientation the effect would be expected to be a maximum. It is obvious that if the basal plane is perpendicular to the length, the orientation of the triangular pattern must be without effect on the longitudinal e.m.f. No correlation whatever was found between the thermal e.m.f. and the orientation of the secondary cleavage plane, thus establishing that within the limits of error indicated by the points in Figure 16 the thermo-electric properties have rotational symmetry about the trigonal axis, as assumed by Kelvin. Of course this proof applies only to bismuth, but it is probable that the other metals have rotational symmetry also. Direct proof would have been much more difficult for any of the others, except for antimony, but the regu-

larity of the results when plotted against only a single parameter, the angle between axis and length, makes it probable that no other parameter enters.

Pressure Coefficient of Resistance. Previously I had measured the effect of pressure on the resistance of two samples of single crystal bismuth,[13] with the basal plane parallel and at 33° to the length. These measurements are now extended to three samples, with the basal plane as 4°, 41°, and 82° to the length. Measurements were made on each of these specimens at 30° and 75° over a pressure range of 12000 kg. The potentiometer method was used as usual. Terminals were soldered to the specimens, so that the following results must be corrected by the change of dimensions to obtain the true relative specific resistances. The accuracy of the measurements was that usual in this work; the average departure of a single reading from a smooth curve for all six runs with three samples was 0.10% of the maximum pressure effect, the extreme variations in accuracy being from 0.02% to 0.15%. Within these limits of error the results can be reproduced by a two-power series in the pressure; this was not the case with the previous measurements. The results follow, pressure being in kg/cm^2:

<div align="center">TABLE II.</div>

Angle between Basal Plane and Length	$\dfrac{\Delta R}{R(0\ 30°)}$	$\dfrac{\Delta R}{R(0\ 75°)}$
4°	$+1.047\times10^{-5}p+2.96\times10^{-10}p^2$	$+1.055\times10^{-5}p+2.67\times10^{-10}p^2$
41°	$+1.564 \qquad +4.93$	$+1.513 \qquad +3.92$
82°	$+2.011 \qquad +8.10$	$+1.975 \qquad +6.14$

The average temperature coefficients between 0° and 100° of these three samples were: 0.00441, 0.00431, and 0.00437 respectively. These values are nearly as high as the best which I have ever obtained for the purest electrolytic bismuth (00441), and are evidence of the high purity of this material. Before the war, the best bismuth which I could get from Kahlbaum had a coefficient of only 0.00332; it is evident that the quality of Kahlbaum's bismuth has improved, or possibly the process of very slow solidification to produce the single crystal itself brings about further purification.

In general, the new results under pressure bear out the results found previously in a narrower range. The pressure coefficient nearly doubles as the cleavage plane changes from parallel to perpendicular to the direction of flow, and except for orientations very close to parallel, the pressure coefficient is less at the higher temperatures. The effect of pressure is therefore to accentuate the excess of resistance across the cleavage planes over that parallel to the planes; one would perhaps be inclined to expect the opposite behavior.

DISCUSSION OF VARIOUS QUESTIONS CONNECTED WITH THE THERMO-ELECTRIC BEHAVIOR OF CRYSTALS.

On the Connection between the Symmetry of the Peltier and Thomson Heats. The conclusion reached in my former paper was that the *total* thermal e.m.f. of a crystal couple need not satisfy Kelvin's law. The total e.m.f. may be analyzed into contributions made by the Peltier heat and the Thomson heat. The conclusion reached in that paper was that the Thomson heat does satisfy Kelvin's law, but that the Peltier heat does not. This conclusion is also substantiated by the new data of this paper, since in the two cases which did not satisfy Kelvin's law, bismuth and tin, the deviation from linearity, which determines the second temperature derivative and so the Thomson heat, was nevertheless linear against $\cos^2\theta$ (or against the specific resistance). We now have to inquire whether this difference between the symmetry of P and σ is a real difference, or whether it is merely apparent, due to the unavoidably greater error in the determination of σ.* There is, of course, a thermodynamic connection between P and σ, namely:

$$\frac{d}{d\tau}\left(\frac{P}{\tau}\right) = \frac{\sigma}{\tau}.$$

Let us now assume that σ satisfies Kelvin's relation, so that we may put $\cdot\sigma = f_1(\tau) + f_2(\tau)\cos^2\theta$, and ask what is thereby involved about the symmetry of P. The equation may be integrated at once, giving:

$$\frac{P}{\tau} = \int_0^\tau \frac{f_1(\tau)}{\tau}\,d\tau + \cos^2\theta \int_0^\tau \frac{f_2(\tau)}{\tau}\,d\tau + \psi(\theta).$$

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* I had gone through considerations of this sort a number of years ago, but had not published them. The importance of the matter was recalled to my attention by a conversation with Dr. Goens in 1926.

$\psi(\theta)$ is an arbitrary function of integration, so that as far as the differential relation between P and σ is concerned, there is no reason why P should be linear in $\cos^2\theta$ at constant temperature merely because σ is.*

But now the third law of thermodynamics suggests that

$$\lim_{\tau=0} \left(\frac{P}{\tau} \right) = 0.$$

Call

$$\lim_{\tau=0} \int_0^\tau \frac{f_1(\tau)}{\tau}\, d\tau = A_1, \quad \text{and} \quad \lim_{\tau=0} \int_0^\tau \frac{f_2(\tau)}{\tau}\, d\tau = A_2,$$

and we have

$$\psi(\theta) = - A_1 - A_2 \cos^2\theta,$$

so that in general:

$$P = \tau \left\{ \left(\int_0^\tau \frac{f_1(\tau)}{\tau}\, d\tau - A_1 \right) + \cos^2\theta \left(\int_0^\tau \frac{f_2(\tau)}{\tau}\, d\tau - A_2 \right) \right\},$$

and at constant temperature this is linear in $\cos^2\theta$. It seems, then, that the third law demands that the Peltier heat satisfy Kelvin's law if the Thomson heat does, and the explanation of the apparent difference in symmetry found experimentally is the greater error of the Thomson heat.

Although the conclusion reached by the argument in the last paragraph appears to me very probable, I do not believe that it can be regarded as entirely rigorous. The question comes in inferring from the third law that P/τ goes to 0 at 0° Abs. Strictly, I suppose that the third law means only that the total entropy change accompanying any finite change in a condensed system at 0° Abs. should vanish. Now consider a couple at 0° Abs. composed of two crystal rods of different orientations. A current may be made to flow in such a system, but the total heat absorbed by the current is necessarily zero because a Peltier heat at one junction is exactly neutralized by a Peltier cold at the other. If the system is so arranged that the Peltier heat arises from the transfer of static charge so that this compensation does not occur, then the system is left charged after the passage of current, and the surface heats of charg-

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* The integration as given is not rigorously exact, because in a non-cubic crystal in which the thermal expansion is different along the different axes $\cos\theta$ is a function of temperature, but the effect is very small.

ing make contributions to the total heat absorbed, so that again the total heat absorbed would be zero.

On the Transverse Thermal Effect, and on Kelvin's Axiom of the Superposition of Heating Effects. Kelvin based his proof of the symmetry of the Peltier heat when a current leaves a crystal surface, and also his proof of the existence and the symmetry of the transverse heating effect,[14] on his so-called "Principle of the Superposition of Thermo-Electric Action," which is: "Each of any number of co-existing systems of electric currents produces the same reversible thermal effect in any locality as if it existed alone." In the paper[15] in which I announced my experimental discovery of the transverse effect,* I stated that Kelvin's principle was internally inconsistent, and that therefore his prediction of the existence of the transverse effect could not be justified. I now find that this statement of mine was not correct, but that if due account is taken of the transverse effect itself, the principle may be maintained and the symmetry relations given by Kelvin are a consequence of the principle.

To straighten the matter out, it will be necessary to go back a considerable distance and correct another erroneous deduction which I made before I knew of the existence of the transverse effect, and which is essentially modified by it.[16] Consider the junction between two metals, one of them a single crystal and the other isotropic, shown in Figure 19. It is evident that thermodynamics requires that the total heat absorbed when a current flows from the single crystal, C, to the isotropic metal, A, in the region at constant temperature, t, be independent of the precise details of the transition

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* When I wrote that paper I supposed that I was the first to find the transverse effect experimentally. Dr. Borelius has, however, recently kindly called my attention to the fact that he and A. E. Lindh described the experimental investigation of this effect in 1917 (Ann. Phys. 53, 97, 1917), in a paper entitled "Resistance, Peltier Heat and Electrical After-Effects, outside and within a Magnetic Field, particularly in Crystalline Bismuth." They made quantitative measurements. I have compared their numerical results with those to be expected from my own measurements of difference of thermo-electric properties of bismuth in different directions, and find agreement within about 30%. The agreement is as good as could be expected in view of the unfavorable dimensions of their specimen, and there can be no doubt that they actually observed the effect. I am sorry that I did not know of their work when I wrote my paper. It is interesting that since I wrote my paper the experimental detection of the effect has also been announced by Terada and Tsutsiu in Japan.

from one metal to the other in the region, so that the total heat absorbed by the current is the same for the two arrangements of the figure. I drew from this the conclusion that the Peltier heat at the surface depends only on the direction of flow of the current within the body of the crystal with respect to the crystal axis, and is independent of the orientation of the surface by which it leaves the crystal. It is now obvious that this conclusion is erroneous, because it neglects the transverse effect at the free surfaces of the crystal. Heat is absorbed when the current passes, not only at
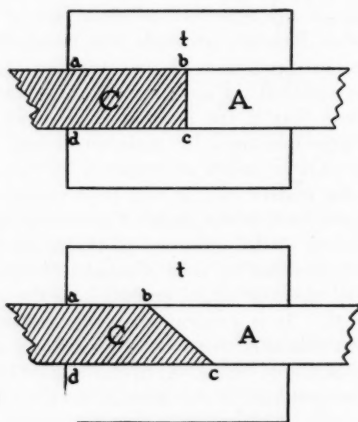

FIGURE 19. Two different methods of making the junction between an isotropic metal and a single crystal in a region at constant temperature. The total heat absorbed by unit quantity of electricity in passing from crystal to isotropic metal is the same in the two arrangements of the figure.

the surface bc which separates the two metals, but also at the transverse surfaces ab and dc. In the upper arrangement of Figure 19, the surfaces ab and dc are equal in extent, and the heat absorbed at ab is exactly neutralized by the heat given out at dc. But in the lower arrangement, this neutralization does not take place. It is evident that the correct theorem is that the total heats absorbed at the surface AB and BC, Figure 20, is equal to that which would be absorbed if the crystal were cut on AC. The heat absorbed at
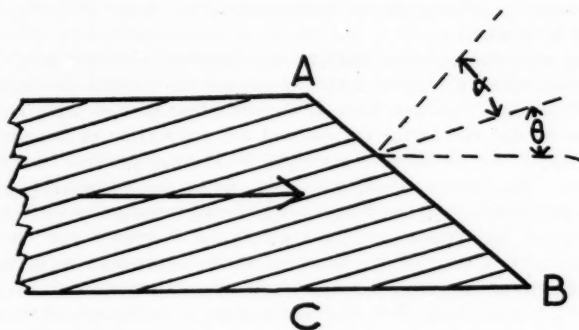
FIGURE 20. Diagram for the calculation of the relation between the reversible heats at various surfaces.

AB is proportional to the total quantity of electricity crossing the surface; hence if we take $AC = 1$, the cross section of the crystal equal to unity, and denote the current density by i, the heat will be merely proportional to i. This heat evidently involves two parameters: θ, the angle which the current within the crystal makes with the crystal axis, and a, the angle between the crystal axis and the normal to the surface. We may, therefore, put for the heat absorbed in unit time at AB, i P (θ, a). The transverse heat absorbed at BC by current parallel to the surface is evidently proportional to current density and the extent of the surface. Call the heat per unit current density per unit area T. T is evidently a function of the angle between the crystal axis and the surface. There is a sign convention that must be observed here. T reverses sign accordingly as the rotation through an acute angle which carries the current (or the surface CB) into the axis carries one inside or outside the crystal. There must also be a sign convention for a. The relation of heat equality is now evidently (since $BC = \tan (a + \theta)$):

$$P(\theta, a) + T(\theta) \tan (a + \theta) \text{ is independent of } a.$$

The sum of these two expressions, or the value of P when $a = -\theta$ $[= P(\theta, -\theta)]$, is what is given by the usual experiments with thermo-couples. In order to find P and T separately, it would

be necessary to experiment with surfaces so large that the heat could be localized.

The conclusion of this analysis is, therefore, that the local heat absorbed when a current leaves a crystal and enters an isotropic conductor is a function both of the direction of flow with respect to the crystal axis in the crystal and the orientation of the surface. Now apply this to Kelvin's principle of the superposition of heating effects. My former proof that this cannot be correct rested on the assumption that the heat absorbed on crossing the surface AB by any of the components into which the current i was resolved was a function only of the direction of the component with respect to the crystal axis, and did not involve the orientation of AB with respect to the axis. But this assumption is erroneous. On using the correct and more general expression above, and also using Kelvin's explicit expressions for P and T

$$\left[\begin{array}{ll} P \equiv P(\theta, -\theta) = P_\perp \cos^2 \theta + P_{11} \sin^2 \theta \\ T(\theta) . \qquad\quad = (P_\perp - P_{11}) \cos \theta \sin \theta \end{array} \right],$$

everything is found to carry through consistently, the total heat is independent of the way in which the current is resolved into components, and the principle of superposition is logically possible.

The only question remaining is, therefore, whether as an experimental fact the symmetry relations of Kelvin are satisfied? We have seen that they are approximately satisfied, but in the case of bismuth and tin, the departures are apparently beyond experimental error. As far as I can see, there is no reason for thinking that the principle must necessarily be satisfied. It is without doubt true, however, that the principle holds to a first approximation in crystals hitherto examined, and in constructing a theory of these effects, it would doubtless be legitimate to begin with this assumption as a first approximation.

The fact that Kelvin's principle can be logically maintained involves a serious modification of a conclusion which I had drawn from my previous experimental results.[17] Granting my previous argument, neglecting the transverse effects, then it was easy to show that Kelvin's principle could be maintained only for one special method of resolving the current, namely parallel and perpendicular to the crystal axis. From the fact that experimentally Kelvin's symmetry relations were approximately satisfied I drew the conclusion that the electrons which constitute the current are actually

compelled to travel either perpendicular or parallel to the crystal axis, by some mechanism more or less of the nature of channels. This conclusion must now be abandoned; from the approximate validity of Kelvin's relation no conclusion whatever can be drawn as to the paths of the electrons.

SUMMARY.

An improved method of making single metal crystals has been developed by which it is possible to cast from the same melt a number of single crystal rods of a wide range of orientation. An apparatus has been developed by which the thermal e.m.f. of 16 rods may be measured simultaneously, so that the only variable factor in the results is the crystal orientation. The thermal e.m.f. between 20° and 88° C of single crystal Zn, Cd, Sb, Sn, and Bi against Cu has been measured, and from the results the thermal e.m.f., Peltier heat, and difference of Thomson heats between rods of the same metal of different orientations is calculated. It is emphasized that in the case of Sb and Bi the heat absorbed by an electron when its direction of motion changes from perpendicular to the axis to parallel to the axis is very large, being respectively 0.2 and 0.4 of the energy of a gas molecule at the same temperature. This is a difficult point for any theory like the recent one of Sommerfeld, in which the part of the energy of an electron which varies with the temperature is supposed small compared with the classical amount. The Kelvin-Voigt law that thermal e.m.f. is a linear function of $\cos^2\theta$, θ being the angle between crystal axis and length of the rod, is verified for Zn, Cd, and Sb, but there are deviations for Sn and Bi which seem distinctly greater than possible experimental error, so that it would appear that in general the Kelvin-Voigt law is only an approximation. Within experimental error the Thomson heat does satisfy the law in all cases; it is only the contribution to total e.m.f. made by the Peltier heat that fails to satisfy the law within experimental error. In the case of Bi a special examination was made of the Kelvin-Voigt assumption that thermal e.m.f. has rotational symmetry about the crystal axis, and no appreciable deviation was found.

The specific resistance of these metals has also been studied as a function of orientation. The possible error from distortion is so great in the case of Cd that a special method of measurement had to be used. The Kelvin-Voigt symmetry relation for resistance is

satisfied within experimental error. Especial attention was given to the resistance of Bi, and the previous low value perpendicular to the cleavage plane verified. The pressure coefficient of resistance of Sb and Bi was redetermined, so that now this quantity is known over the entire range of orientation.

In the theoretical discussion it is shown that the third law of thermodynamics gives considerable plausibility, although not complete certainty, to the thesis that the symmetry of the Peltier and the Thomson heat must be the same; this means that the apparent experimental difference in the symmetry of the two heats is merely an effect of the much greater error in the Thomson heat. It is shown that, contrary to the statements previously made by me, Kelvin's axiom of the superposition of thermal effects of currents is not internally inconsistent, so that his proofs of the symmetry relations and of the existence of a transverse temperature effect are logically possible. Experiment, however, seems opposed to the truth of the axiom. The revised discussion further shows that the surface heat where a current leaves a metal crystal is a function both of the direction of flow with respect to the crystal axis within the crystal and of the orientation of the surface, contrary to my former statement. It is also shown that these crystal phenomena no longer offer a basis for a proof that the electrons must move in the crystal along something analogous to fixed channels.

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